Out-Diffusion and Precipitation of Copper in N- and P-Type Silicon

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Abstract

The use of copper for metallic interconnects in ULSI technology has revived the interest in the precipitation kinetics of copper in silicon. We have investigated copper of various contamination levels in n- and p-type silicon. While the interstitial copper concentration was measured with Transient Ion Drift (TID), the precipitated copper concentration was detected by X-Ray Fluorescence (XRF). The existence of the precipitates as well as their morphology was investigated by Transmission Electron Microscopy (TEM). In n-type silicon no interstitial copper was detected, whereas the concentration of precipitated copper was close to the copper solubility at the diffusion temperature. Contrary, in p-type silicon interstitial copper was observed after quench, and only few copper precipitates were found if the copper contamination was chosen below a certain critical level, which was found to be in the range of $10^{16} cm^{-3}$. At higher contamination levels, precipitation prevails and the concentration of precipitated copper reaches the solubility level at the diffusion temperature. Despite the difference in the precipitation kinetics of p- and n-type silicon, the precipitates found in p-type form the same thin {111}-platelets as are known after quench in n-type. Analysis of the experimental data suggests that the copper kinetics is dominated by bulk precipitation in n-type silicon and by out-diffusion in p-type silicon. If the concentration of the positively charged copper exceeds the acceptor concentration, type inversion may occur. We discuss a possible Fermi level effect as a criteria for out-diffusion and precipitation.

Introduction

Introduction of copper interconnects in silicon integrated circuit technology has drastically increased the danger of unintentional introduction of copper into silicon substrates. Consequently, understanding of the behavior of copper in silicon and evaluation and prediction of its potential effect on device performance has become an increasingly important problem of semiconductor materials science and device technology. The experience of copper research accumulated in the past 35 years has demonstrated that the task of understanding the physical properties of copper in silicon is much more difficult than for most other transition metals. This is caused by interstitial copper being positively charged in silicon [1] and retaining a high diffusivity in the silicon lattice even at room temperature [2]. Copper homogeneously distributes in the bulk of the wafer during high temperature anneals and forms interstitial point defects, complexes, precipitates, or diffuses to the surface of the wafer upon cooling down. The detrimental effect of copper to devices depends on which of these reaction paths becomes preferential. Thus, prediction of the detrimental role of copper in integrated circuits and evaluation of the feasibility of its gettering require fundamental physical understanding of properties of copper in silicon. The previous attempts to solve this fundamentally challenging and technologically relevant problem met with only limited success, mainly because none of the groups involved in copper research had the combination of analytical tools necessary to access copper in all possible states and to follow its reaction from the interstitial state to a stable state in the lattice.

Today two mechanism of copper in silicon are proposed. Since the 1980s Transmission electron microscopy (TEM) studies suggested that in n-type silicon most of copper precipitates in the bulk after high-temperature anneal and quench to form Cu_3Si platelets on the {111} planes. Comparison of the electrical properties of these platelets as measured with Deep Level Transient Spectroscopy (DLTS) and computer simulations of the resulting spectra have revealed that these precipitates form band like states within the band gap of the silicon matrix ranging from E_C-0.35eV to E_C-0.15eV [3]. Furthermore, they show that the copper precipitates are positively charged if the Fermi level is below their neutrality level at E_C-0.2eV and neutral or positively charged if the Fermi level is above this critical level. However, recent experimental studies of Shabani *et al*. [4] and McCarthy *et al*. [5] demonstrated another possible behavior of copper, copper diffusing to the surface within 48 to 72 hours after high temperature in-diffusion of copper into p-type samples. In n-type silicon, out-diffusion was observed only if the sample temperature was raised to 300^0C-400^0C in a second annealing step. Up to now no explanation for this difference in the behavior of copper in n-type silicon and p-type silicon could be provided as to what is the reaction path of copper in silicon, what is the reason for the difference in its behavior in n-type and p-type silicon.

During the last two years, our research team achieved significant progress in studies of interstitial copper in silicon. We introduced Transient Ion Drift (TID) as a technique that is capable of measurements of low concentrations of interstitial copper in the bulk of silicon [6]. Complementary, copper precipitates can be detected and mapped by X-Ray Florescence (XRF). Utilizing the synchrotron-based XRF microprobe at the ALS copper bulk concentration of 10^{16} cm^{-3} can be measured. This corresponds to the observation of isolated copper precipitates with a diameter of 20nm, or smaller precipitates with a higher density [7]. The research reported here utilizes the unique experimental capabilities of our group and the ALS to investigate the properties of copper in silicon in order to approach the first comprehensive and predictive model of the behavior of copper.

Results and Discussion

In Fig. 1 we plot the maximum interstitial copper concentration as measured with TID vs the solubility of copper at in-diffusion temperature. The copper has been introduced into the silicon wafer by in-diffusion at high temperatures followed by a quench.

Three different p-type samples are presented with a doping concentration of $4*10^{14}$, $4*10^{15}$ and $2*10^{16}$ boron atoms per cm^3, respectively. A most significant effect is the observation of two regimes: A lower copper contamination regime and a higher copper contamination regime. In the lower copper contamination regime, up to a critical copper solubility concentration at diffusion temperature in the range of 10^{16} cm^{-3}, the maximum interstitial copper concentrations as measured with TID increases with the solubility concentration. However, beyond that critical copper contamination level the interstitial copper concentration decreases with increasing solubility concentration. The critical amount of in-diffused copper is identical for the samples doped with $4*10^{14}$ to $4*10^{15}$ boron atoms per cm^3 and is found to be at $1*10^{16}$ copper atoms per cm^3. Nevertheless, the critical concentration of copper contamination is shifted to $3*10^{16}$ copper atoms per cm^3 for the sample doped with $2*10^{16}$ boron atoms per cm^3.

In Fig. 2 we plot the concentration of precipitated copper as measured with XRF vs the solubility of copper at diffusion temperature for one n-type sample doped with $2*10^{15}$ phosphorus atoms per cm^3 and three p-type samples with doping concentrations again ranging from 10^{14} to 10^{16} boron atoms per cm^3. Because of the detection limit of XRF only samples with an initial contamination of at least 10^{16} copper atoms per cm^3 are measured. It can be seen that the amount of precipitated copper for the n-type sample follows the solubility concentration of
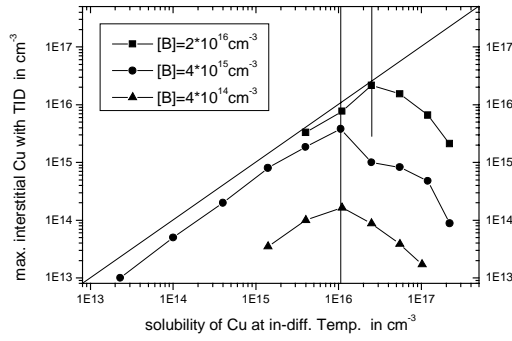
Fig. 1: Interstitial copper concentration as measured with TID for boron doped samples of $4 \cdot 10^{14}$ cm^{-3}, $4 \cdot 10^{15}$ cm^{-3} and $2 \cdot 10^{16}$ cm^{-3}.
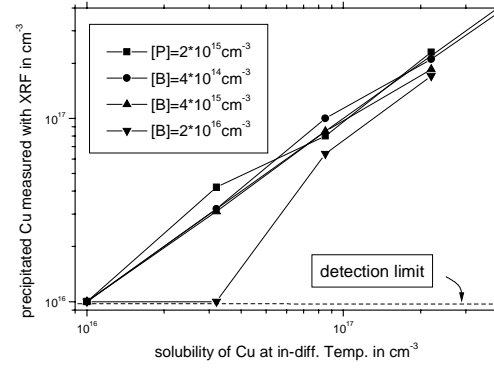
Fig. 2: Precipitated copper concentration as measured with XRF for a phosphorus doped sample of $2 \cdot 10^{15}$ cm^{-3} and for boron doped samples of $4 \cdot 10^{14}$ cm^{-3}, $4 \cdot 10^{15}$ cm^{-3} and $2 \cdot 10^{16}$ cm^{-3}.

copper at diffusion temperature. The same is true for the p-type samples with boron concentrations of 10^{14} cm^{-3} and 10^{15} cm^{-3}. The concentration values of precipitated copper are very homogeneously distributed as measured with the XRF microprobe with a spatial resolution of about 1 μm^2. In particular no profile of precipitated copper has been found. This indicates that all the copper that has been in-diffused has precipitated in the bulk very fast. On the contrary, the detected concentrations of precipitated copper for the sample doped with $2*10^{16}$ boron atoms per cm^3 does not follow the solubility concentration of copper at in-diffusion temperature. Only if the initial copper concentration is above the critical copper concentration for this particular sample of $3*10^{16}$ cm^{-3}, as found in Fig. 1, the amount of precipitated copper equals the in-diffused concentration of copper. Yet, after in-diffusion of copper to an amount that equals the critical concentration of this sample the concentration of precipitated copper is below the detection limit, i.e. much below its initial concentration. Thus the difference of copper between the initial copper concentration and the later found concentration of precipitated copper has diffused out of the sample.

This data show that for silicon doped with $2*10^{16}$ boron atoms per cm^3 out-diffusion is dominant for the lower copper contamination regime and precipitation is the dominant reaction path for the higher copper contamination regime. Unfortunately the detection limit of XRF equals the critical copper concentration of the lower doped samples, i.e. the samples doped with less than 10^{16} boron atoms per cm^{-3}. Therefore we can only measure the precipitated copper concentration for the higher copper contamination regime of these samples. We see that for the lower doped samples, as was observed for the higher doped sample, precipitation is dominant if the initial copper concentration is above the critical copper concentration of these samples. Yet, with TID we recognize a qualitative similar behavior of the copper in both regimes for all p-type wafers. This suggests that for the lower doped samples the lower contamination regime is also dominated by out-diffusion. Future work at the ALS with a lower XRF-detection limit for copper in silicon, as is intended, will be able to decide about this behavior for low doped samples.

The question that remains is why is out-diffusion being the dominant path in the lower copper contaminated region, and why does copper "change its mind" and precipitation becomes the dominant reaction path in the higher copper contaminated region? A hypothesis, which was put forward in our recent conference presentations [8, 9] is that the coulomb repulsion between positively charged copper ions and positively charged copper precipitates in p-Si might retard copper precipitation. The precipitation becomes possible in n-type silicon or in p-type silicon if the position of the Fermi level determined by the concentration of shallow dopants and copper

donors becomes so high in the band gap that either copper ions or copper precipitates change the sign of their charge and coulombic repulsion between the two disappears. This hypothesis represents a principally new physical mechanism, which was never discussed before with applications to copper, and is one of the issues to be addressed in future experiments.

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